UDC 666.653:666.3.03:621.9.048.7

NEW METHODS FOR DEVELOPMENT OF THREE-DIMENSIONAL CERAMICS BASED ON BARIUM HEXAFERRITE WITH CHROMIUM ADDITIVES

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Translated from Steklo i Keramika, No. 6, pp. 14 – 18, June, 2003.

The possibility of implementing a reaction of self-propagated high-temperature synthesis of ferrites controlled through selective laser treatment is demonstrated. The conditions of synthesis of barium hexaferrite with a chromium additive and the effect of additional annealing on the results of synthesis are investigated. The three-dimensional ceramic products obtained have sufficiently good consumer properties.

The method of laminar selective laser sintering (SLS) or fusion of powder composites allows for the development of functional three-dimensional articles, whose physicomechanical and physicochemical properties may differ significantly from the properties of the initial powder mixture. The SLS method differs from other fast-prototyping methods in that one can immediately use the results of sintering without substantial expenses on subsequent treatment, and also in the fact that new phases are synthesized in nonequilibrium fast laser heating – cooling conditions. The topical problems include the search for new powder compounds and media to obtain objects with prescribed characteristics in sintering and the research of sintering specific in such media.

Contemporary electrical engineering requires a wide range of specialized construction materials with special properties relative to electromagnetic fields. Ferromagnetic materials based on Ba + metal find wide application as permanent magnets, in SHF technologies, and in electronic devices [1] The traditional process of producing ferrites includes the stages of ferrite powder preparation from the respective metal oxides or thermal decomposition of metal salts thorough subsequent milling, mixing, compression, sintering (firing) at high temperatures, and molding of intermediate pieces. Besides, the high temperatures of salt decomposition reactions can be implemented using self-propagating high-temperature synthesis (SHS) [2].

The difficulties of producing hexaferrites with reproducible properties are mainly related to the nature of these materials, which are phases of variable compositions. Many properties of ferrites depend not only on the ratio of the main components, but also on the thermodynamic parameters of synthesis, of which the most important are the temperature and pressure of oxygen in the gaseous phase. Furthermore, some physical characteristics of ferrites are structure-sensitive and depend on the conditions of structure formation in sintering and structure modifications in the presence of microimpurities or in additional thermal treatment. An increase in the sintering temperature and the cooling rate, which takes place in laser treatment, and a reducing atmosphere raise the content of Fe^{2+} in the ferrite structure and decrease its resistivity.

The idea of combining the SHS and SLS processes in the same technological cycle was analyzed in [3]. Note that combining the SHS and SLS processes is hard to control. The start of the SHS reaction can be before or after the proper sintering process. In such case the initial components will be burned (or insufficiently burned). Therefore, the main problem in laser synthesis of ferrites is precise selection of the laser treatment schedule, in which both process (SHS and SLS) would exist in dynamic equilibrium. We have earlier demonstrated the fundamental possibility of implementing a controlled SHS reaction in the course of SLS of individual layers for the purpose of obtaining ferrite phases of the type of $Li_{0.5}Fe_{2.5-x}Cr_xO_4$ and $BaFe_{12x}Cr_xO_{19}$ [4].

It is known that introduction of chromium cations improves the magnetic properties of barium hexaferrite [2]. The purpose of our study was to investigate the condition of SLS of three-dimensional articles made from a powder mixture of barium and iron oxides with a chromium additive and identify the laser treatment parameters, which would provide for the production of required phases in a combination of SLS and SHS, as well as studying the effect of additional annealing on the results of synthesis of hexaferrite phases. X-ray structure analysis made it possible to identify the phase com-

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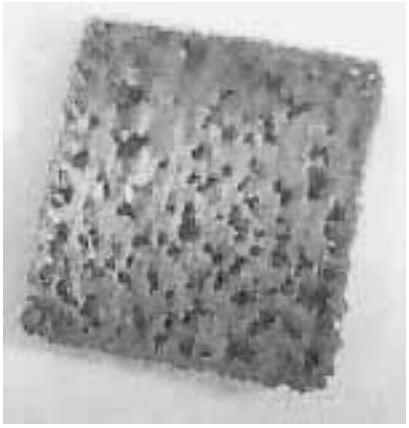

Fig. 1. Sintered single layer (mixture 3). Laser treatment power 14.3 W, laser radiation scanning velocity 21 mm/sec.

position of products synthesized, whereas magnetic measurements identified the volume magnetic parameters of three-dimensional articles produced by the SLS method.

The testing unit for SLS of powder compositions included a laser based on YAG : Nd^{3+} (Kvant-60, radiation wavelength 1.064 μm) operating continuously; deflectors for scanning laser radiation over the surface; a PC to control the process; detachable lenses with a focal length of 149 and 336 mm (laser beam diameter in focus: d_b = 50 and 100 μm, respectively); a mechanism for depositing and smoothing powder mixtures; a cylindrical platform shifting vertically. The proper SLS process and the testing unit scheme were described in detail earlier [3]. The scanning rate of laser radiation over surface v could vary within wide limits, and the laser power P varied from 0.5 to 21.0 W. Laser treatment of mixtures was performed in air with d_b = 50 μm.

In accordance with recommendations in [2], the following powder mixtures were prepared for the synthesis of barium hexaferrite:

1) $BaO_2 + Fe_2O_3 + Cr_2O_3 + Fe = 1.0 : 2.5 : 1.0 : 5.0$;
2) $BaCO_3 + Fe_2O_3 + Cr_2O_3 + Fe = 1.0 : 2.5 : 1.0 : 5.0$;
3) BaO_2 + Fe (PZh RNL-A) + $Cr_2O_3 = 1.0 : 3.3 : 1.8$.

All initial oxide powders and iron powder were of the "chemically pure" grade, and fusing powder PZh RNL-A contained up to 95% Fe and plating additives. Barium carbonate was obtained in the following substitution reaction:

$$Na_2CO_3 + Ba(NO_3)_2 = BaCO_3 + 2NaNO_3.$$

As SLS took place in air, it is assumed that oxygen is present in reactant mixtures 1 – 3 and should intensely diffuse into the end product at high temperatures.

The microstructures sintered were investigated using an MBS-9 and a Neophot-30 optical microscopes. Magnetic measurements were carried out on a EG&G PARC M4500 magnetometer equipped with an electric magnet with induction up to 1 T. X-ray phase analysis of the surface of sintered samples was carried out on a DRON-2.0 diffractometer with copper and cobalt K_α nonfiltered radiation.

The laser treatment power and the laser beam scanning rate varied during the synthesis. The main sintering parameters were the thickness of an individual sintered powder layer z, its strength parameters, and presence of deformations (visually). The latter is undesirable, as this would later prevent efficient sintering of the layers to each other during laminar SLS of volumetric products. Powder mixtures subjected to treatment in synthesis of individual layers were freely poured in a volume clearly larger than the laser sintering depth of a single layer. A controlled regime was understood as implementation of the SHS exothermic reaction precisely inside the laser-radiated spot (known as the diffusion regime of SHS). Three samples were sintered for each schedule in the presence of a constant magnetic field and in its absence. It was assumed that the presence of a magnetic field would contribute to ordering of the ferromagnetic components of the initial mixture and would facilitate a more homogenous structure of the sintered layer.

Searching for optimum sintering conditions demonstrated that P from 10 to 20 W with v from 57 to 10 mm/sec is preferable for mixtures 1 and 2. Under low power (up to 10 W) and high radiation scanning velocities (higher than 60 mm/sec) the laser energy is insufficient for sintering, and single layers disintegrate upon touching. In contrast, low scanning velocities (higher than 10 mm/sec) or high power (higher than 20 W) lead to a deformation of the individual layer. Uncontrolled SHS (thermal explosion) was never observed within the specified power and scanning velocity ranges. Insignificant luminescence was visible in the spot of laser treatment under the specified regimes, which we attributed to heat emission in the course of the exothermic SHS reaction. However, subsequent laminar synthesis of volumetric articles from mixtures 1 and 2 using the optimum SLS conditions for single layers did not produce good results. Either individual layers easily separated from each other, breaking the shape of the volumetric product, or deposition of subsequent layers became impossible.

Sintering of powder mixture 3 made it possible not only to obtain strong single layers but also to synthesize three-dimensional articles (parallelepipeds with a surface area of 100 mm^2 and 5 – 10 mm high). This can be attributed to the presence of plating additives in iron power PZh RNL-A. Figure 1 shows the photo of a sintered layer. The dynamics of single layer depth variations depending on the power and velocity of laser treatment are shown in Figs. 2 and 3. It can be seen that the variation of z on the whole agrees with the presented data.

As a consequence of studies using optical metallography, it was found that the surface of sintered samples has the extended porosity and metallic luster typical of iron melt (Fig. 4). Analysis of the macrostructure indicated that porosity increases significantly with increasing power of laser treatment. To produce a more homogeneous surface structure

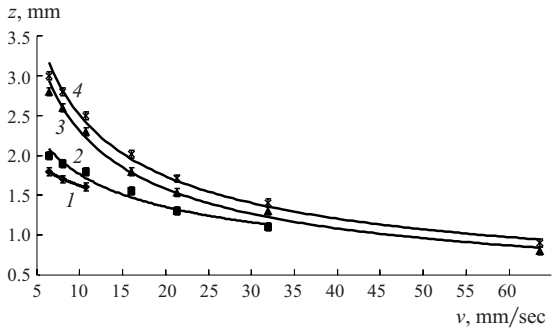

Fig. 2. Dependence of sintered layer thickness on scanning velocity of laser radiation (mixture 3) under fixed laser power equal to 7.1 (*1*), 11.3 (*2*), 14.3 (*3*), and 15.0 W (*4*).

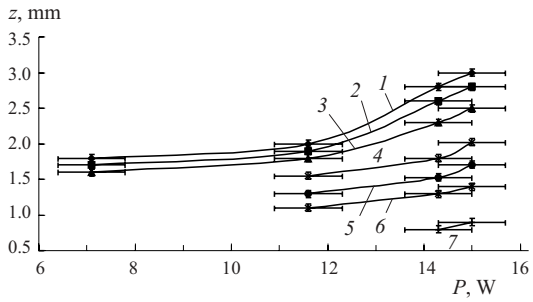

Fig. 3. Dependence of sintered layer thickness on laser power (mixture 3) under a fixed scanning velocity of laser radiation equal to 6.14 (*1*), 8.0 (*2*), 10.7 (*3*), 16.0 (*4*), 21.3 (*5*), 31.9 (*6*), and 63.6 mm/sec (*7*).

and to have good magnetic properties, "soft" laser regimes are preferable. Although intense energy emission in laser treatment increases the sintering depth (Fig. 1), its structural heterogeneity grows (Fig. 4) and the strength of the obtained ferrites decreases.

X-ray diffraction studies of the products of sintering (mixtures 1 and 2) revealed the presence of the following phases in their structure: $BaFe_{0.72}Fe_{0.28}O_{2.64}$, $BaCrO_{2.9}$, $Ba_5Fe_{14}O_{26}$, and $BaFe_{0.5}Fe_{0.5}O_{2.25}$, as well as simple oxides Fe_2O_3 and Cr_2O_3. A double pass of the laser beam over the surface in sintering single layers increases the relative intensity of the x-ray lines of $BaCrO_{2.9}$, $Ba_3Fe_2O_6$, and $BaFe_{0.5}Fe_{0.5}O_{2.25}$ and decreases the quantity of oxides, whereas the magnetic field used in SLS increases as well the content of the specified ferrite phases, although insignificantly.

Tables 1 and 2 show the variation of the peak intensity of sintered products after SLS of mixture 3 as a function of the laser regime.

It can be seen from Table 1 that with increasing scanning velocity (i.e., with decreasing quantity of energy transmitted by the laser to the powder volume being sintered), the relative intensity of the phase $BaFe_2O_4$ decreases and that of the phase $BaFe_{12}O_{19}$ increases. The line related to this phase can be interpreted as well as phase $BaFe_{12x}Cr_xO_{19}$ [2].

For a constant laser radiation velocity, an increase in power increases the relative intensity of the line related to the phase $BaFe_2O_4$ and decreases the intensity of the line of phase $BaFe_{12}O_{19}$.

Additional thermal annealing of synthesized three-dimensional articles was performed for 2 h at temperatures of 1070 and 1470 K. Qualitative x-ray diffraction analysis indicated that the content of the ferrite phases $BaFe_{0.72}Fe_{0.28}O_{2.64}$, $BaFe_{0.24}Fe_{0.76}O_{2.88}$, $BaCrO_{2.9}$, $Ba_5Fe_{14}O_{26}$, $Ba_3Cr_2O_6$ and $BaFe_{12}O_{19}$ increases to 80 – 100%, whereas oxide phases totally disappear.

The composition of initial powder mixtures, the laser sintering conditions, and additional annealing have a perceptible effect on the magnetic properties of synthesized ferrites. Figure 5 shows the results of measuring the hysteresis loop σ (H) of single ferrite layers sintered from mixtures 2 and 3 depending on the laser treatment regime and the presence of a constant magnetic field in synthesis. Variations of laser radiation power and presence of a magnetic field have no effect

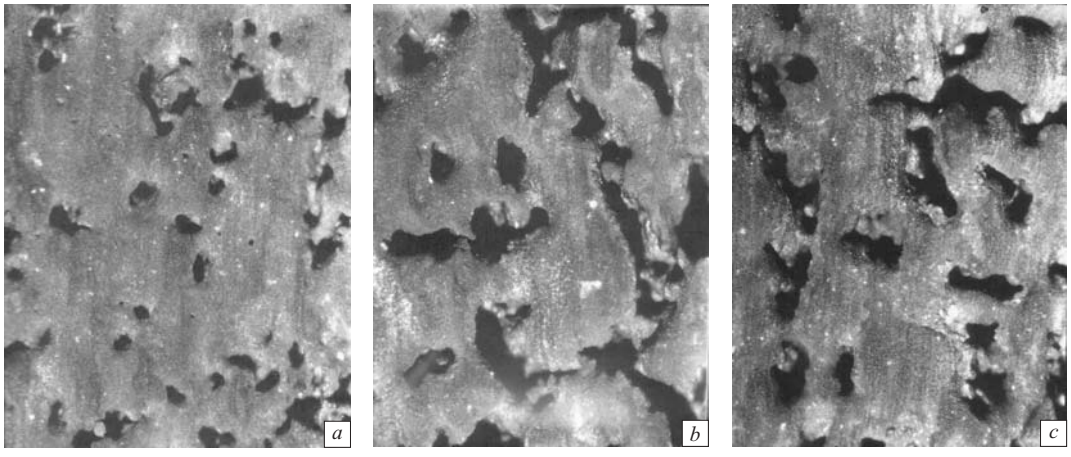

Fig. 4. Macrostructure of the surface of sintered single layers (mixture 3) under laser radiation scanning velocity of 32 mm/sec and laser power 11.6 (*a*), 15.0 (*b*), and 14.3 W (*c*) (× 20).

TABLE 1

Phase	I/I_m* for laser radiation scanning velocity, mm/sec		
	21.3	31.9	63.6
$BaFe_2O_4$	100	39	43
Cr_2O_5	50	64	49
$(CrFe)_2O_3$	0	74	65
$BaFe_{12}O_{19}$	0	18	19

* Laser power 15 W.

TABLE 2

Phase	I/I_m* for laser treatment power, W		
	11.6	14.3	15.0
$BaFe_2O_4$	35	56	100
Cr_2O_5	70	67	61
$(CrFe)_2O_3$	92	8	74
$BaFe_{12}O_{19}$	20	8	0

* Laser radiation scanning velocity 21.3 mm/sec.

on the shape and location of the hysteresis loop with respect to the coordinate origin. The coercive force is not high and the shape of the curve is far from rectangular (compared with the results in [2]). The general tendencies are as follows (Table 3): the presence of a magnetic field in SLS decreases the degree of magnetic saturation and increases the degree of residual magnetization, which presumably is due to higher structural ordering.

Use of iron oxide substantially increases residual induction and saturation induction, whereas the coercive force virtually does not change. The differences in the magnetic properties of hexagonal barium ferrite earlier obtained by the SHS method from the properties of samples in the present study are probably due to their higher porosity.

Additional thermal annealing changes not only the ratio of the phases but also the magnetic properties of the samples

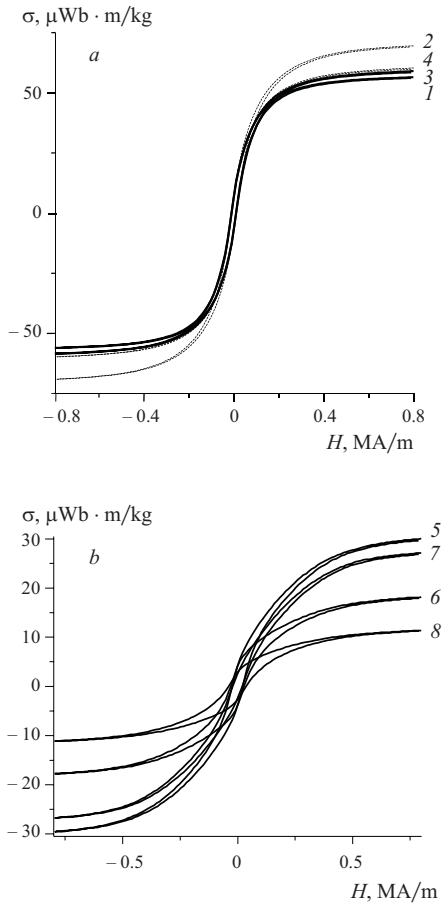

Fig. 5. Hysteresis loops for single layers synthesized from mixtures 2 (*a*) and 3 (*b*). Curve numbers correspond to SLS regimes listed in Table 3.

synthesized (Fig. 6). Samples after firing at 1470 K have perceptibly higher coercive force and good rectangularity of the hysteresis loop, which is essential for practical use. At the same time, these samples typically have a lower degree of magnetization. It should be noted that thermal annealing levels the differences in the laser treatment modes (Figs. 5*b*

TABLE 3

SLS regime number	Laser power, W	Laser radiation scanning velocity, mm/sec	Maximum degree of magnetization, μWb · m/kg	Degree of residual magnetization, μWb · m/kg	Coercive force, kA/m	Rectangularity of hysteresis loop
			Mixture 2			
1	15.2	57.0	61.1	11.5	20.2	0.18
2	15.2 + magnetic field	57.0	62.0	12.3	22.6	0.19
3	19.9	57.0	62.4	12.4	22.4	0.20
4	19.9 + magnetic field	57.0	62.0	11.4	19.4	0.18
			Mixture 3			
5	14.4	63.6	30.1/38.0/7.4*	4.20/5.21/4.49	23.7/23.40/222	0.14/0.14/0.61
6	14.4	16.0	18.2/8.33/7.81	4.15/2.88/4.85	29.8/32.2/190	0.23/0.35/0.62
7	14.4 + magnetic field	63.6	27.2/13.1/4.09	2.59/1.88/2.35	21.6/20.2/203	0.10/0.14/0.57
8	14.4 + magnetic field	16.0	11.3/6.49/5.3	2.91/2.23/3.24	36.5/40.2/172	0.26/0.34/0.61

* First number) initial value; second number) after annealing at 1070 K; third number) after annealing at 1470 K.

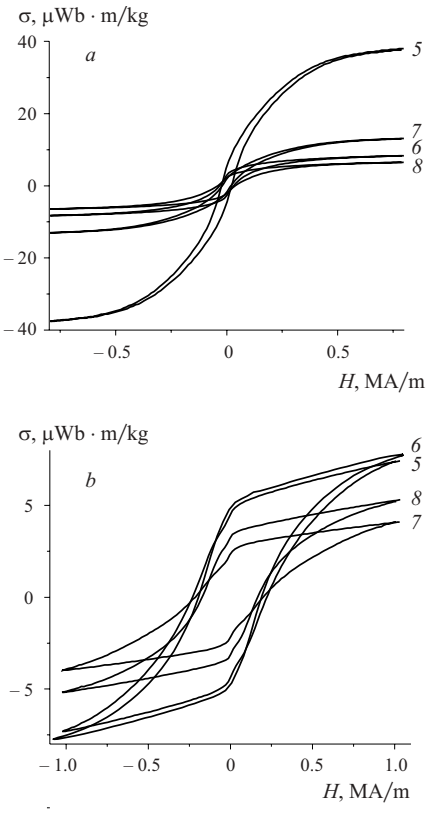

Fig. 6. Hysteresis loops for volume samples after annealing at temperatures 1070 K (*a*) and 1470 K (*b*). Curve numbers correspond to SLS regimes listed in Table 3.

and 6). Furthermore, the strength of ferrites after each additional annealing grows significantly.

The present study has investigated the conditions of SLS of three-dimensional articles from powder mixtures of barium and iron oxides with chromium additives and the laser treatment parameters that allow for producing hexaferrite phases combining the SLS and SHS processes. The phase composition of the products obtained has been identified and the volumetric magnetic characteristics of articles synthesized by SLS have been determined.

REFERENCES

1. *Powder metallurgy. Materials, Technologies, Properties, Application Areas. A Reference Book* [in Russian], Naukova Dumka, Kiev (1985).
2. M. V. Kuznetsov, L. F. Barquin, Q. U. Pankhurst, and I. P. Parkin, "Self-propagating high-temperature synthesis of barium-chromium ferrites $BaFe_{12x}Cr_xO_{19}$ ($0 < x < 6.0$)," *J. Phys. D: Appl. Phys.*, **32**, 2590 – 2598 (1999).
3. I. V. Shishkovskii, A. G. Makarenko, and A. L. Petrov, "Studies of the conditions of SHS of intermetallic compounds during SLS of powder compositions," *Fiz. Goreniya Vzryva*, **35**(2), 59 – 64 (1999).
4. I. V. Shishkovsky, S. E. Zakiev, Yu. B. Scheck, et al., "Selective laser-assisted sintering of SHS-ferrites in powder systems based on Ba – Fe and Li – Fe compositions," in: *Modern Problems of Combustion and its Applications, IV School-Seminar*, Minsk (2001), pp. 59 – 62.